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Hydrocarbon Surface Chemistry on Si(100)

by

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Hydrocarbon Surface Chemistry on Si(100)

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Abstract

The interaction of various hydrocarbon species with the Si(100) surface has been investigated using several surface science techniques. The efficiency of carbon deposition is related to the efficiency of SiC thin film formation. The hydrocarbon species studied include acetylene (C_2H_2), ethylene (C_2H_4), and the adsorbed methyl group ($CH_3(a)$). In the case of the chemisorption of acetylene and ethylene, the π -bond of the olefinic molecules interacts with the dimer unit (Si_2) on the Si(100)-(2x1) surface. One monolayer of both acetylene and ethylene on Si(100) has been achieved by saturating the surface at 105 K, and a di- σ bonding structure is proposed for one molecule per Si_2 dimer unit at monolayer coverage. Upon heating, the majority (> 95 %) of the adsorbed acetylene undergoes dissociation to produce chemisorbed carbon and $H_2(g)$. In contrast, chemisorbed ethylene desorbs intact from Si(100) at ~ 550 K, with approximately 2 % of the monolayer undergoing dissociation. The low activation energy for desorption ($E_d^*(C_2H_4) = 38 \text{ kcal mol}^{-1}$) allows C_2H_4 to desorb prior to significant decomposition.

Investigations of the thermal behavior of $CH_3(a)$ on Si(100) show that the adsorbed methyl group is stable up to ~ 600 K.

At higher temperatures, $\text{CH}_3(\text{a})$ decomposes to $\text{CH}_x(\text{a})$ ($x < 3$) species, and subsequently liberates $\text{H}_2(\text{g})$, leaving carbon on the surface. Less than 1 % of the adsorbed carbon species (CH_x , $x \leq 3$) desorbs in the form of C_2 hydrocarbon species upon heating. This indicates that the methyl group is an efficient source of surface carbon by thermal decomposition.

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1. INTRODUCTION

The mechanism by which a molecule interacts with a crystalline semiconductor surface is of fundamental importance in semiconductor technologies. Various vapor deposition methods and epitaxial growth procedures are largely dependent on the interaction of gaseous molecules with the substrate surface. Knowledge of the nature of the elementary chemical processes at the surface, and the bonding structure as well as the chemical nature of the chemisorbed species is therefore important.

The adsorption and thermal behavior of hydrocarbon molecules on well-defined silicon surfaces is of considerable interest since such species are used in the formation of SiC thin films[1-10] or in epitaxial diamond film growth [11]. This paper is a review of our investigations of the interaction of various hydrocarbon species with the Si(100) surface [12-17]. It is known that the reconstructed Si(100) surface consists of parallel rows of Si₂ dimers with one dangling bond on each surface Si atom. As a result of Si dimerization, a (2x1) superlattice is observed by low energy electron diffraction (LEED) [18], and by scanning tunneling microscopy (STM) [19]. The study of the chemisorption of a number of hydrocarbon molecules on the Si(100) surface has shown that the π -bond in an unsaturated hydrocarbon is the active center for reaction of these molecules with a clean Si(100) surface [20]. In contrast, the saturated hydrocarbon molecules, containing only single bonds (σ -bonds) between

carbon atoms, do not react with the clean Si(100) surface at low temperatures [20].

The hydrocarbon species studied in this work include acetylene (C_2H_2) [12,15], ethylene (C_2H_4) [12-14], and the adsorbed methyl group ($CH_3(a)$), produced by dissociative adsorption of CH_3I [16,17]. Various surface science techniques have been employed, including quantitative uptake measurements, temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and vibrational spectroscopy. Both C_2H_2 and C_2H_4 are studied because of the multiple carbon-carbon bonds in these two molecules and also because both molecules have been used in the growth of SiC films [2-6,10]. One monolayer of both acetylene and ethylene on Si(100) has been achieved by saturating the surface at 105 K, and a di- σ bonding structure is proposed for one molecule per Si_2 dimer unit at monolayer coverage. Upon heating, the majority (> 95 %) of the adsorbed acetylene undergoes dissociation to produce chemisorbed carbon and $H_2(g)$. In contrast, chemisorbed ethylene does not dissociate appreciably on Si(100) and desorbs intact at ~ 550 K.

The methyl radical is also generally considered as an active species for carbon deposition using plasma sources as well as in high temperature CVD reactors [9,11]. Our investigations of the thermal behavior of $CH_3(a)$ on Si(100) show that the adsorbed methyl group is stable up to ~ 600 K. At higher temperatures, $CH_3(a)$ decomposes to $CH_x(a)$ ($x < 3$) species. Combining the results from AES and TPD studies, we

conclude that the methyl group is an efficient source of surface carbon by thermal decomposition.

2. EXPERIMENTAL

The ultrahigh vacuum (UHV) system (with a base pressure of 1×10^{-10} Torr) and the Si(100) crystal preparation have been described previously [12-16]; selected aspects will be summarized here. The system is equipped with an Auger electron spectrometer, an argon ion sputtering gun, a collimated and calibrated microcapillary array doser [21], and a multiplexed quadrupole mass spectrometer (QMS) with capabilities for both random flux and line-of-sight detection [22]. Heating of the Si(100) crystal (15 x 15 x 1.5 mm; p-type; B-doped; 10 Ω -cm) is provided by a Honeywell programmable temperature controller used to drive a feedback circuit to control the power to the crystal [23].

For the adsorption of molecular species, a calibrated microcapillary array doser was used to deliver the gas molecules onto the Si(100) surface [21]. The doser contains an internal pinhole aperture (2 μ m diameter) whose conductance has been calibrated accurately for the molecular species to be studied [12]. The partial pressure change of the molecular species during adsorption was monitored by the mass spectrometer with the shield open and in a random flux detection geometry. Using the same mass spectrometer

(differentially-pumped), TPD measurements can be made with the shield closed and in a line-of-sight detection geometry.

Surface cleanliness and the relative coverages of adsorbates were verified by AES. All the AES data reported here were obtained by averaging at four or more positions on the prepared surface. In addition, a second UHV chamber, equipped with a high resolution electron energy loss spectrometer (HREELS), is used for the surface vibrational spectroscopic studies [17]. The typical primary beam energy used for HREELS measurements is 4.2 eV with a full width at half maximum of 65-70 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1 Absolute coverage measurements for C_2H_2 and C_2H_4

Figure 1(A) shows a schematic diagram of the apparatus employed to measure the absolute coverage of adsorbate during the adsorption process. A collimated beam of molecular species is delivered from a doser containing a microcapillary collimator array. The absolute flux of the collimated beam onto the crystal surface is determined from the calibrated conductance through the internal pinhole aperture [12] and from the calculated angular distribution of the beam [24]. Before the measurement, the cleaned Si(100) crystal is placed in a known position relative to the doser, and a movable shutter is placed between the doser and the crystal to separate the crystal from the direct beam. After a flux of gas molecules has been established through the doser, the shutter

is then moved out of the beam and adsorption begins to take place on the surface. The gas molecules which miss the crystal, or which strike the crystal and do not adsorb, are measured with the shielded QMS which detects only the random flux of non-adsorbed species. For a detailed description of the measurement method, the interested reader is referred to References 12 and 25.

A typical adsorption measurement for C_2H_2 on $Si(100)-(2 \times 1)$, at a crystal temperature of 105 K, is shown in Figure 1(B). When the shutter is moved out of the beam, the partial pressure of C_2H_2 detected by the mass spectrometer decreases instantly, from P_1 to P_2 , indicating that the adsorption of C_2H_2 onto the $Si(100)$ surface occurs. The fraction of gas molecules striking the surface and adsorbing can be determined by the ratio of $(P_1 - P_2)/(P_1 - P_0)$, which is 0.45 ± 0.01 for C_2H_2 . This is in excellent agreement with the calculation which shows that the fraction of the beam intercepted by the crystal is 0.46 ± 0.05 , based on the known doser and crystal geometry [24]. This indicates the initial C_2H_2 sticking probability. $S(0)$, is nearly unity at 105 K. Knowing the absolute flux, F , and the sticking probability, $S(t)$, the absolute coverage, $N(t)$, in the time interval t can be directly determined from the kinetic uptake curve (as shown in Figure 1(B)) according to the following equation,

$$N(t) = F \int S(t) dt.$$

With an additional small correction in the low sticking probability region (the region where the adsorption efficiency is beyond the detection limit of the mass spectrometer) [12], we have determined that the saturation coverage of C_2H_2 on the $Si(100)-(2 \times 1)$ surface is $2.5(\pm 0.2) \times 10^{14}$ molecules/cm². Using the same measurement, an identical saturation coverage has been determined for C_2H_4 on $Si(100)$ at 105 K. On a perfect reconstructed $Si(100)-(2 \times 1)$ surface, the dimer density is 3.4×10^{14} Si_2 dimers/cm². However, a high density of defects, like missing dimers, are generally seen on an UHV-prepared surface [19]. Missing dimer defects were also suggested to stabilize the $Si(100)$ reconstruction [26]. STM measurements often shows a 5-10 % defect density on $Si(100)$ surface. Since other studies have shown that defects are inactive for olefin adsorption [27], the saturation capacity of $Si(100)$ will be reduced in proportion to the defect density. Assuming a 10 % defect density, the saturation coverage on non-defective $Si(100)$ sites is near unity (0.8 ± 0.07), i.e., our measurements suggest that each Si_2 dimer site adsorbs a single C_2H_2 or C_2H_4 molecule. This chemisorption model, which involves the formation of Si-C bonds between the carbon atom pair of the chemisorbed olefinic molecule and the silicon atom pair in a Si_2 dimer, is supported by the preservation of the (2×1) LEED pattern upon chemisorption of C_2H_2 and C_2H_4 , by HREELS measurements [28,29], and by thermodynamic arguments [14,15].

3.2 Thermal behavior of chemisorbed C_2H_2 and C_2H_4

Thermal desorption studies for both C_2H_2 and C_2H_4 on Si(100) reveal that the only desorption products are the intact molecules (C_2H_2 and C_2H_4) and H_2 . TPD spectra obtained after saturating the Si(100) surface with C_2H_2 and C_2H_4 are shown in Figures 2(A) and 2(B), respectively. Using the analytical method developed by Chan, Aris, and Weinberg [30], the activation energy for desorption (E_d) and the pre-exponential factor (k_d) can be determined by using the full-width-half-maximum of the desorption peaks. This analysis was performed for various initial coverages. Assuming first-order desorption kinetics, E_d and k_d in the zero-coverage limit for both molecules are: $E_d^*(C_2H_2) = 46.1 \pm 2.0$ kcal/mol, $k_d^*(C_2H_2) = 2 \times 10^{13 \pm 1} \text{ s}^{-1}$ [15]; and $E_d^*(C_2H_4) = 38.0 \pm 1.5$ kcal/mol, $k_d^*(C_2H_4) = 5 \times 10^{13 \pm 0.5} \text{ s}^{-1}$ [14].

Also measured was the thermal desorption of molecular hydrogen, which is evolved from thermal decomposition of the chemisorbed hydrocarbon molecules (Figure 2). This desorption feature occurs at $T \geq 700$ K which is near that for H_2 desorption from the monohydride phase (H-Si-Si-H) on Si(100). Based on the magnitude of the H_2 desorption signals, the extent to which the chemisorbed hydrocarbon molecules has decomposed on the Si(100) surface during heating can be estimated. By comparing the yield of H_2 desorption from a saturated overlayer of C_2H_2 with that from a saturated monohydride phase (the amount of H_2 desorbed from the saturated monohydride phase corresponding to 1 monolayer (ML)=

6.8×10^{14} H/cm² [31]), the integrated area of H₂ desorption from decomposition of C₂H₂ is estimated to be ~78 % of 1 ML. For a C₂H₂ coverage of 0.8 ± 0.07 ML, this therefore indicates that the major reaction pathway for chemisorbed C₂H₂ on Si(100) is thermal decomposition of C₂H₂ with subsequent hydrogen desorption; and only a small fraction of C₂H₂ desorbs as the intact molecule (Figure 2(A)). A similar analysis has been done for the thermal desorption of C₂H₄ on Si(100). In contrast to the thermal behavior of chemisorbed C₂H₂, the measurements indicate that approximately 98 % of the chemisorbed C₂H₄ desorbs as intact molecules without decomposition (Figure 2(B)) [32].

The conversion of chemisorbed hydrocarbon to surface carbon was also investigated using AES. In Figure 3, the ratios of C(KLL) to Si(LVV) signals indicate that the amount of carbon retained on the surface is a function of the crystal temperature. Heating of a C₂H₂ saturation overlayer through the C₂H₂ desorption temperature results in a ~5 % decrease of the C/Si Auger intensity ratio as judged by the averaged data in Figure 3. This confirms the TPD measurements which show that the desorption process is a minor reaction pathway for C₂H₂ on Si(100). Heating above ~800 K causes the C(KLL) signal to decrease as carbon diffuses into the bulk. Qualitatively, similar results have been reported for the decomposition of propylene (H₂C=CH-CH₃) on Si(100) with subsequent carbon penetration at higher temperatures [27]. On the other hand, investigation of thermal behavior of C₂H₄ on Si(100) using AES

shows that the carbon coverage decreases distinctly at ~550 K, and has dropped to nearly zero by ~600 K [14]. This corresponds to the temperature range in which C₂H₄ desorption occurs (Figure 2(B)).

The information contained in Figures 2 and 3 shows that chemisorbed C₂H₄ decomposes very inefficiently on Si(100), in sharp contrast to chemisorbed C₂H₂ which dehydrogenates nearly completely (> 95 %). The main difference between the interaction of these two molecules with the Si(100) surface is the activation energy for desorption: $E_d^*(C_2H_2) = 46.1 \pm 2.0$ kcal/mol; $E_d^*(C_2H_4) = 38.0 \pm 1.5$ kcal/mol, which produces a ~160 K difference in desorption temperature. The low desorption activation energy for C₂H₄ allows the adsorbed C₂H₄ to desorb at a lower temperature prior to significant decomposition, whereas the high desorption activation energy for C₂H₂ causes the adsorbed C₂H₂ to be retained on the surface to a higher temperature where dehydrogenation dominates the surface process. In addition, mechanistic studies using the isotopic mixing method (¹³C₂H₄ and ¹²C₂H₄) have shown that less than 1 % isotopic mixing of ethylene occurs in the temperature range of 500 K ~ 950 K where the desorption and decomposition of C₂H₄ takes place [13]. This observation excludes the remote possibility that C₂H₄ desorption is via the scission of the carbon-carbon bond, followed by recombination of CH₂(a) fragments. We therefore conclude that the low probability of SiC film growth at elevated temperatures as previously reported (the efficiency

of SiC formation using C_2H_4 is $\sim 10^{-3}$ per collision at 940 K [3,13]) is mainly due to nondissociative behavior and desorption of C_2H_4 , rather than to inefficient C_2H_4 chemisorption. In fact, studies of the growth of a β -SiC film on Si surfaces have shown that the growth rate obtained using C_2H_2 was larger than that obtained using C_2H_4 in an UHV environment [10].

3.3 Thermal behavior of adsorbed CH_3

The thermal stability of the adsorbed methyl group on Si(100) was studied by using the dissociative chemisorption of methyl iodide (CH_3I) as a source of $CH_3(a)$. Experimental evidence, based on both quantitative uptake measurements (the method described in section 3.1) and TPD, indicates that the CH_3I molecule dissociates into a covalently bonded methyl group and an iodine atom upon adsorption at 300 K [16]. Heating causes the decomposition of the adsorbed methyl group. Figure 4 shows typical TPD spectra from CH_3I on Si(100). The main features observed are 2 amu (H_2^+ from H_2 desorption) and 127 amu (I^+ from both HI and I desorption). The desorption of C_2 hydrocarbon species (data not shown), occurring in the same temperature range as the H_2 desorption peak, was also observed. The amount of the adsorbed carbon species desorbing in the form of C_2 hydrocarbon species was estimated to be less than 1 % [16]. In addition, neither the desorption of methane nor the desorption of CH_3I was observed. These results suggest that $CH_3(a)$ on Si(100) is stable up to ~ 600 K. At higher

temperatures, the adsorbed methyl group decomposes and liberates $H_2(g)$.

The thermal stability of $CH_3(a)$ on $Si(100)$ has also been witnessed by vibrational spectroscopy using HREELS [17]. Figure 5 shows the vibrational spectra obtained after the CH_3I adlayer on $Si(100)$ was heated to the indicated temperatures. Characteristic $C-H_x$ ($3 \geq x \geq 1$) vibrational modes are observed in three regions: the C-H stretching modes in the $2800-3200\text{ cm}^{-1}$ region, and the C-H deformation modes in the $1100-1600\text{ cm}^{-1}$ and $700-1000\text{ cm}^{-1}$ regions [33,34]. The vibrational spectrum shown in Figure 5(A) was obtained after CH_3I adsorption at 300 K. In addition to the CH_x vibrational modes, the presence of the Si-I stretching vibration at 435 cm^{-1} and the absence of the C-I stretching mode at 525 cm^{-1} confirm that CH_3I dissociates into $CH_3(a)$ and $I(a)$ at 300 K. Identical spectra were observed by heating the surface up to 600 K. Further heating to 700 K (Figure 5(C)) causes two pronounced changes in the vibrational spectrum: (1) a large intensification of the Si-H mode at 2140 cm^{-1} ; and (2) a new frequency mode developing at 980 cm^{-1} . The appearance of the Si-H mode at 700 K suggests that the adsorbed methyl group has begun to decompose to $CH_2(a)$ and/or $CH(a)$ species. This is also supported by the development of the new vibrational feature at 980 cm^{-1} which can be assigned to either a CH_2 rocking mode [33] or to a C-H deformation mode [34,35]. The vibrational spectrum recorded after heating to 775 K (Figure 5(D)) shows that all the CH_3 and CH_2 deformation modes in the

1100-1600 cm^{-1} region have disappeared, indicating the decomposition of all the $\text{CH}_3(\text{a})$ and $\text{CH}_2(\text{a})$ species. In addition, the presence of $\text{CH}(\text{a})$ up to 775 K is indicated by the $\delta(\text{C-H})$ bending deformation at 945 cm^{-1} and the attenuated C-H stretching mode at 2970 cm^{-1} . By 850 K, only a 770 cm^{-1} vibrational loss remains which is due to carbon on the surface [36]. These results provide the direct evidence for the thermal stability of $\text{CH}_3(\text{a})$ on $\text{Si}(100)$.

The lack of a desorption pathway ($< 1\%$) for chemisorbed $\text{CH}_x(\text{a})$ ($x \leq 3$) species suggests that the efficiency for the conversion of the $\text{CH}_x(\text{a})$ species to surface carbon is near unity. Figure 6 shows the thermal effect on both carbon and iodine Auger intensities. The change of carbon Auger intensity is negligible up to ~ 760 K when a monolayer produced from CH_3I is examined. At higher temperatures, diffusion of surface carbon into the bulk is observed as shown by the decrease of the carbon Auger intensity. The iodine signal, on the other hand, begins to decrease at ~ 700 K and becomes undetectable above 900 K. The decrease of iodine Auger intensity is consistent with the thermal desorption of iodine and hydrogen iodide shown in Figure 4. Combining these results with TPD and HREELS studies, we therefore conclude that the methyl group is an efficient source for carbon deposition on $\text{Si}(100)$.

Finally, the general observation of carbon diffusion at $T \geq 800$ K (Figures 3 and 6, and Ref. 27) suggests that a supply of surface Si can be achieved by heating during SiC thin film growth process. In fact, it has been shown, for the reaction

of Si(100) with C₂H₄, that the formation of a SiC film only occurs at $T \geq 940$ K [5]. In addition, it was found that the surface of the growing film was covered with a Si layer, indicating that surface aggregation of bulk Si on top of the growing SiC film occurs [5]. Recently, the epitaxial growth of SiC crystals has been achieved from the reaction of Si(100) with a low flux beam of C₂H₂ ($< 6 \times 10^{15}$ molecules s⁻¹ cm⁻²) at 1100 - 1300 K. These studies also confirmed that the surface under reaction conditions was covered with a Si-rich layer [2].

4. SUMMARY

The adsorption and thermal behavior of various hydrocarbon species (C₂H₂, C₂H₄, and CH₃(a)) on the Si(100)-(2x1) surface have been investigated. The major findings are summarized below:

(1) A quantitative uptake measurement method has been developed using an accurately calibrated beam doser and a shielded QMS for random flux detection. The results of the C₂H₂ (C₂H₄) chemisorption on Si(100) at 105 K show that the chemisorbed C₂H₂ (C₂H₄) forms a saturated monolayer with one C₂H₂ (C₂H₄) per Si₂ dimer site, producing a di- σ surface complex.

(2) Chemisorbed C₂H₂ predominantly undergoes dehydrogenation, leading to carbon deposition. A minor reaction pathway (≤ 5 %) involves desorption of C₂H₂ with an activation energy at the zero-coverage limit (E_d^0) of 46

kcal/mol. In contrast, chemisorbed C_2H_4 desorbs predominantly without appreciable dissociation. The relatively low binding energy for C_2H_4 , as suggested from its low activation energy for desorption ($E_d^\circ(C_2H_4) = 38$ kcal/mol), allows the chemisorbed C_2H_4 to desorb at a lower temperature prior to significant C-H bond activation.

(3) The adsorbed methyl group on Si(100) is stable up to ~ 600 K. At higher temperatures, $CH_3(a)$ decomposes to $CH_x(a)$ ($x < 3$) species and subsequently liberates $H_2(g)$, leaving carbon on the surface. The lack of a desorption pathway ($< 1\%$) for chemisorbed $CH_x(a)$ ($x \leq 3$) allows the $CH_x(a)$ species to decompose completely, suggesting that the methyl group is an efficient source for carbon deposition.

(4) The general observation of carbon diffusion into the bulk at $T \geq 800$ K (Figures 3 and 6, and Ref. 27) suggests that a supply of surface Si for epitaxial growth of SiC can be achieved by heating during the growth process.

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REFERENCES

1. J.A. Powell, J.B. Petit, J.H. Edgar, I.G. Jenkins, L.G. Matus, J.W. Yang, P. Pirouz, W.J. Choyke, L. Clemen, and M. Yoganathan, Appl. Phys. Lett. 59, 333 (1991).
2. I. Kusunoki, M. Hiroi, T. Sato, Y. Igari, and S. Tomoda, Appl. Surf. Sci. 45, 171 (1990).
3. P.A. Taylor, M.J. Bozack, W.J. Choyke, and J.T. Yates, Jr, J. Appl. Phys. 65, 1099 (1989).
4. C.D. Stinespring, A. Freedman, and J.C. Wormhoudt, Mat. Res. Soc. Symp. Proc. 131, 227 (1989).
5. F. Bozso, J.T. Yates, Jr., W.J. Choyke, and L. Muehlhoff, J. Appl. Phys. 57, 2771 (1985).
6. P. Liaw and R.F. Davis, J. Electrochem. Soc. 132, 642 (1985).
7. A. Addamiano and J.A. Sprague, Appl. Phys. Lett. 44, 525 (1984).
8. S. Nishino, J.A. Powell, and H.A. Will, Appl. Phys. Lett. 42, 460 (1983).
9. Y. Catherine, G. Turban, and B. Grolleau, Thin Solid Films 76, 23 (1981).
10. I.H. Khan and R.N. Summergrad, Appl. Phys. Lett. 11, 12 (1967).

11. For a recent review of diamond growth, see J.C. Angus and C.C. Hayman, *Science* 241, 913 (1988).
12. C.C. Cheng, R.M. Wallace, P.A. Taylor, W.J. Choyke, and J.T. Yates, Jr., *J. Appl. Phys.* 67, 3693 (1990).
13. C.C. Cheng, W.J. Choyke, and J.T. Yates, Jr., *Surf. Sci.* 231, 289 (1990).
14. L. Clemen, R.M. Wallace, P.A. Taylor, M.J. Dresser, W.J. Choyke, W.H. Weinberg, and J.T. Yates, Jr., *Surf. Sci.* 268, 205 (1992).
15. P.A. Taylor, R.M. Wallace, C.C. Cheng, W.H. Weinberg, M.J. Dresser, W.J. Choyke, and J.T. Yates, Jr., *J. Am. Chem. Soc.* in press.
16. H. Gutleben, S.R. Lucas, C.C. Cheng, W.J. Choyke, and J.T. Yates, Jr., *Surf. Sci.* 257, 146 (1991).
17. M.L. Colaiaanni, P.J. Chen, H. Gutleben, and J.T. Yates, Jr., *Chem. Phys. Lett.* 191, 561 (1992).
18. J.A. Appelbaum and D.R. Hamann, *Surf. Sci.* 74, 21 (1978).
19. (a) R.J. Hamers, R.M. Tromp, and J.E. Demuth, *Phys. Rev. B* 34, 5343 (1986); (b) R.M. Tromp, R.J. Hamers, and J.E. Demuth, *Phys. Rev. Lett.* 55, 1303 (1985).
20. M.J. Bozack, P.A. Taylor, W.J. Choyke, and J.T. Yates, Jr., *Surf. Sci.* 177, L933 (1986).
21. M.J. Bozack, L. Muehlhoff, J.N. Russell, Jr., W.J. Choyke, and J.T. Yates, Jr., *J. Vac. Sci. Technol.* A5, 1 (1987).
22. V.S. Smentkowski and J.T. Yates, Jr., *J. Vac. Sci. Technol.* A7, 3325 (1989).

23. R.J. Muha, S.M. Gates, J.T. Yates, Jr., and P. Basu, Rev. Sci. Instrum., 56, 613 (1985).
24. (a) C.T. Campbell and S.M. Valone, J. Vac. Sci. Technol. A3, 408 (1985); (b) A. Winkler and J.T. Yates, Jr., J. Vac. Sci. Technol. A6, 2929 (1988).
25. (a) D.A. King and M.G. Wells, Surf. Sci. 29, 454 (1972); (b) T.E. Madey, Surf. Sci. 33, 355 (1972).
26. K.C. Pandey, in Proceedings of the Seventeenth International Conference on the Physics of Semiconductors, edited by D.J. Chadi and W.A. Harrison, P.55, Springer-Verlag, New York, 1985.
27. M.J. Bozack, W.J. Choyke, L. Muehloff, and J.T. Yates, Jr., Surf. Sci. 176, 547 (1986).
28. J. Yoshinobu, H. Tsuda, M. Onchi, and M. Nishijima, J. Chem. Nishijima, J. Yoshinobu, H. Tsuda, and M. Onchi, Surf. Sci. 192, 383 (1987).
30. C.-M. Chan, R. Aris, and W.H. Weinberg, Appl. Surf. Sci. 1, 360 (1978).
31. C.C. Cheng and J.T. Yates, Jr., Phys. Rev. B 43, 4041 (1991).
32. Figure 2 is shown for hydrogen-containing hydrocarbons for simplicity. The amount of the decomposed ethylene based on the molecular hydrogen desorption was estimated from measurements using perdeuteroethylene (C_2D_4) (see Ref. 14).
33. R.T. Conley, Infrared Spectroscopy, Allyn and Bacon, Newton, 1972.

34. L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1975.
35. F. Lee, A.L. Backman, R. Lin, T.R. Gow, and R.I. Masel, *Surf. Sci.* 216, 173 (1989).
36. J.A. Stroscio, S.R. Bare, and W. Ho, *Surf. Sci.* 154, 35 (1985).

FIGURE CAPTIONS

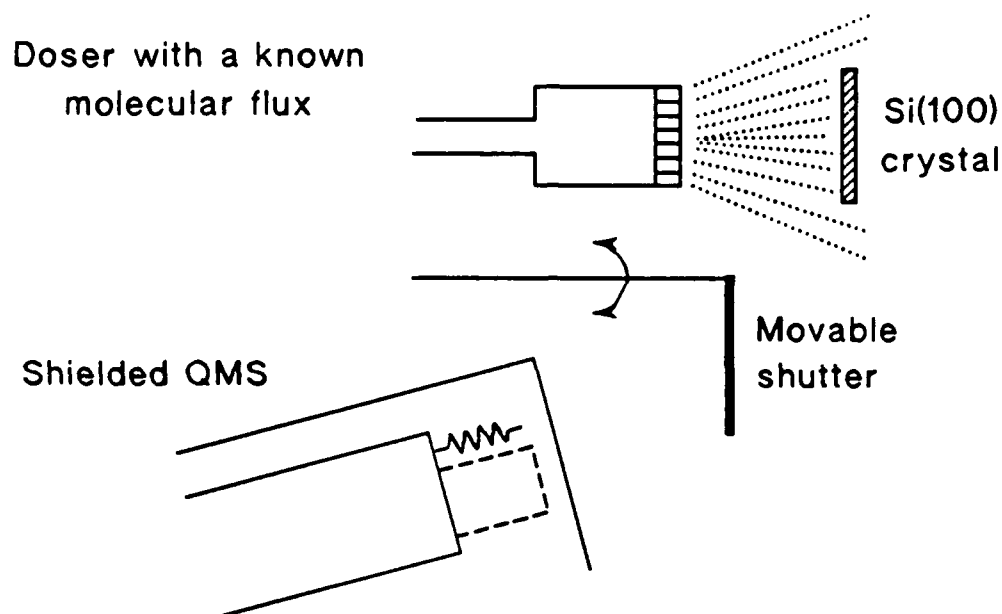
- Figure 1. (A) Schematic diagram of apparatus for quantitative uptake measurements; (B) A typical kinetic uptake measurement for C_2H_2 on Si(100) at 105 K.
- Figure 2. TPD spectra obtained after saturating the Si(100) surface with C_2H_2 (A) and C_2H_4 (B). The heating rate for the TPD measurements was 1.0 K/s. Note that the desorption spectrum of $C_2H_2^+/C_2H_2$ is amplified by a factor of 5.
- Figure 3. The change in carbon Auger intensity upon annealing a C_2H_2 adlayer to different temperatures on Si(100). The error bars represent a $\pm 1 \sigma$ deviation from the average of six AES measurements on the surface.
- Figure 4. Typical TPD spectra from CH_3I on Si(100) with a heating rate of 1.0 K/s.

Figure 5. Vibrational spectra of CH_3I adsorbed on $\text{Si}(100)$ at 300 K, followed by sequential heating to the indicated temperatures with a heating rate of 1 K/s. All HREEL spectra were recorded after cooling to 100 K.

Figure 6. Thermal effects on adsorbed CH_3I on $\text{Si}(100)$ using AES. The Auger intensities are normalized to the intensities of the saturated adlayer. Lines are drawn to guide the eye.

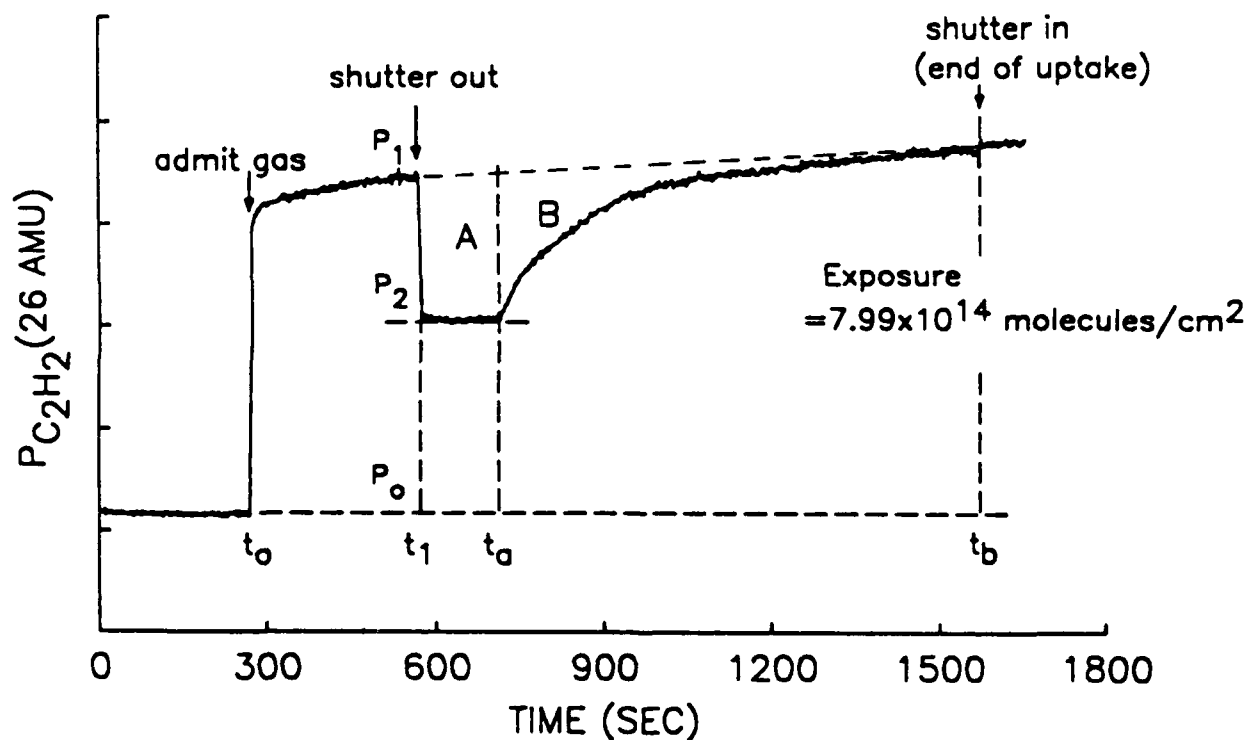
(A)

Schematic of Uptake Measurement



(B)

ADSORPTION OF C_2H_2 ON Si(100) SURFACE AT 105K

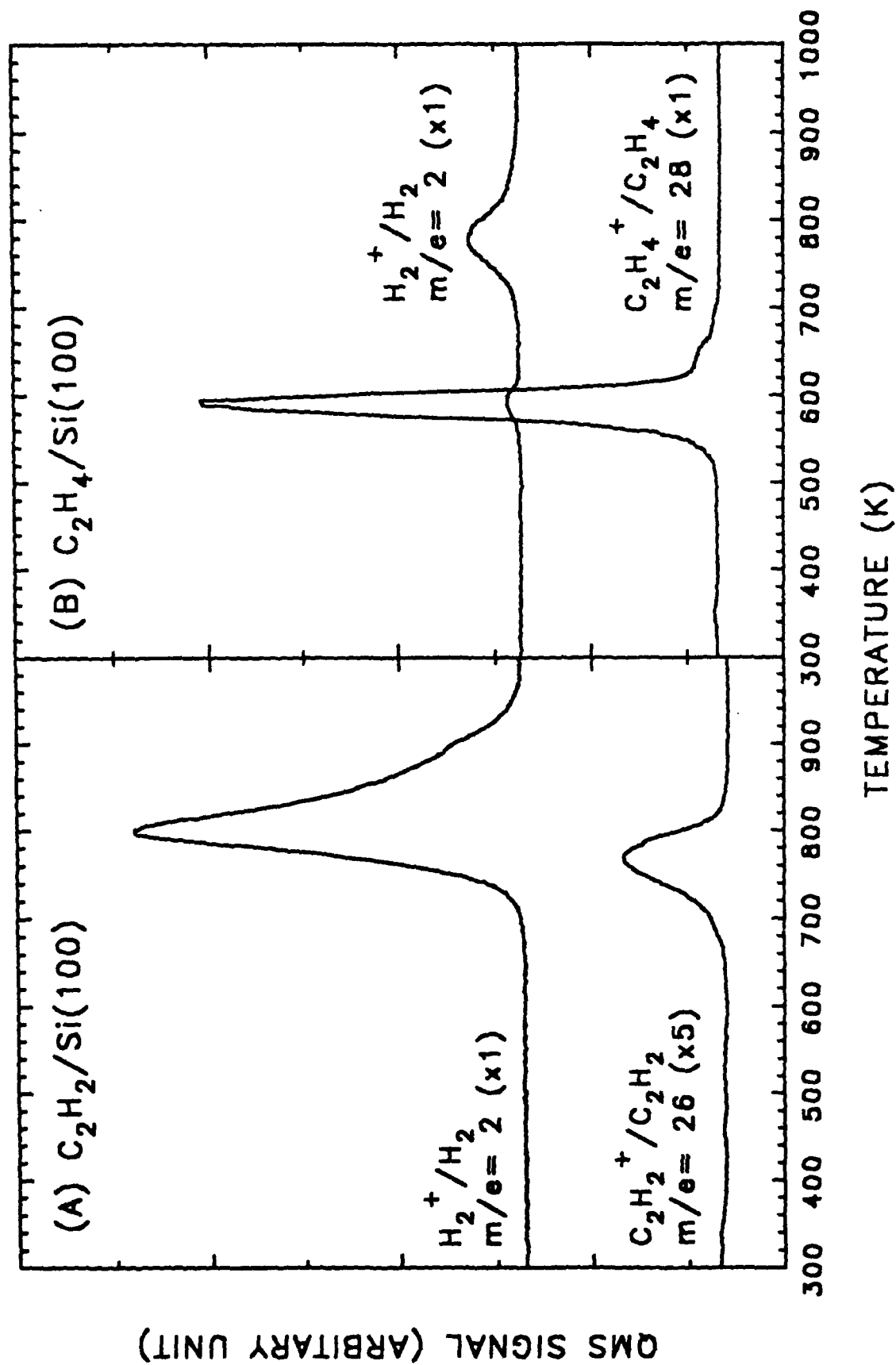


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Figure 1

TPD SPECTRA OF C_2H_2 AND C_2H_4 ON $Si(100)$ —(2x1)

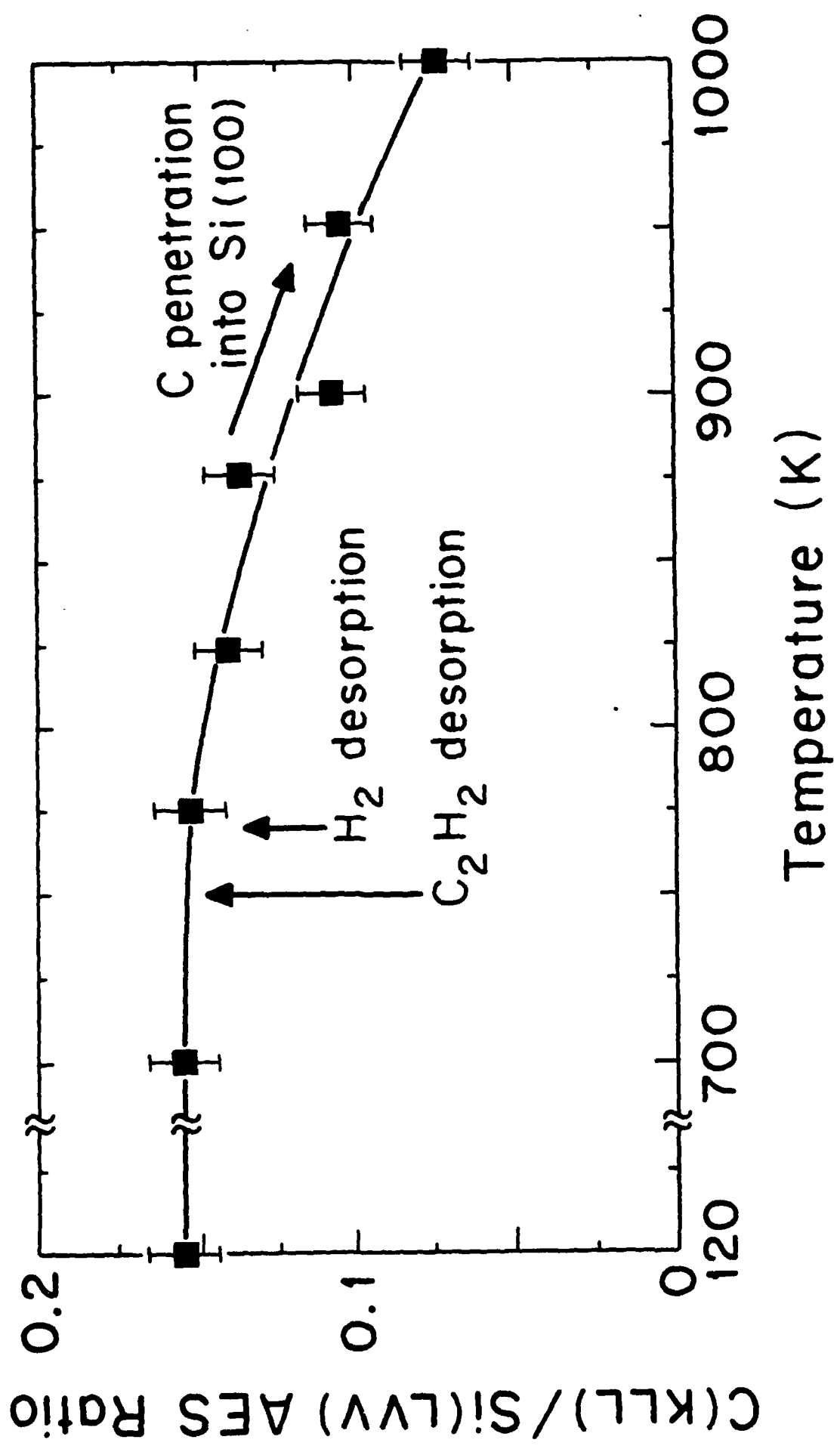
AT SATURATION COVERAGE; $dT/dt = 1.0$ K/s



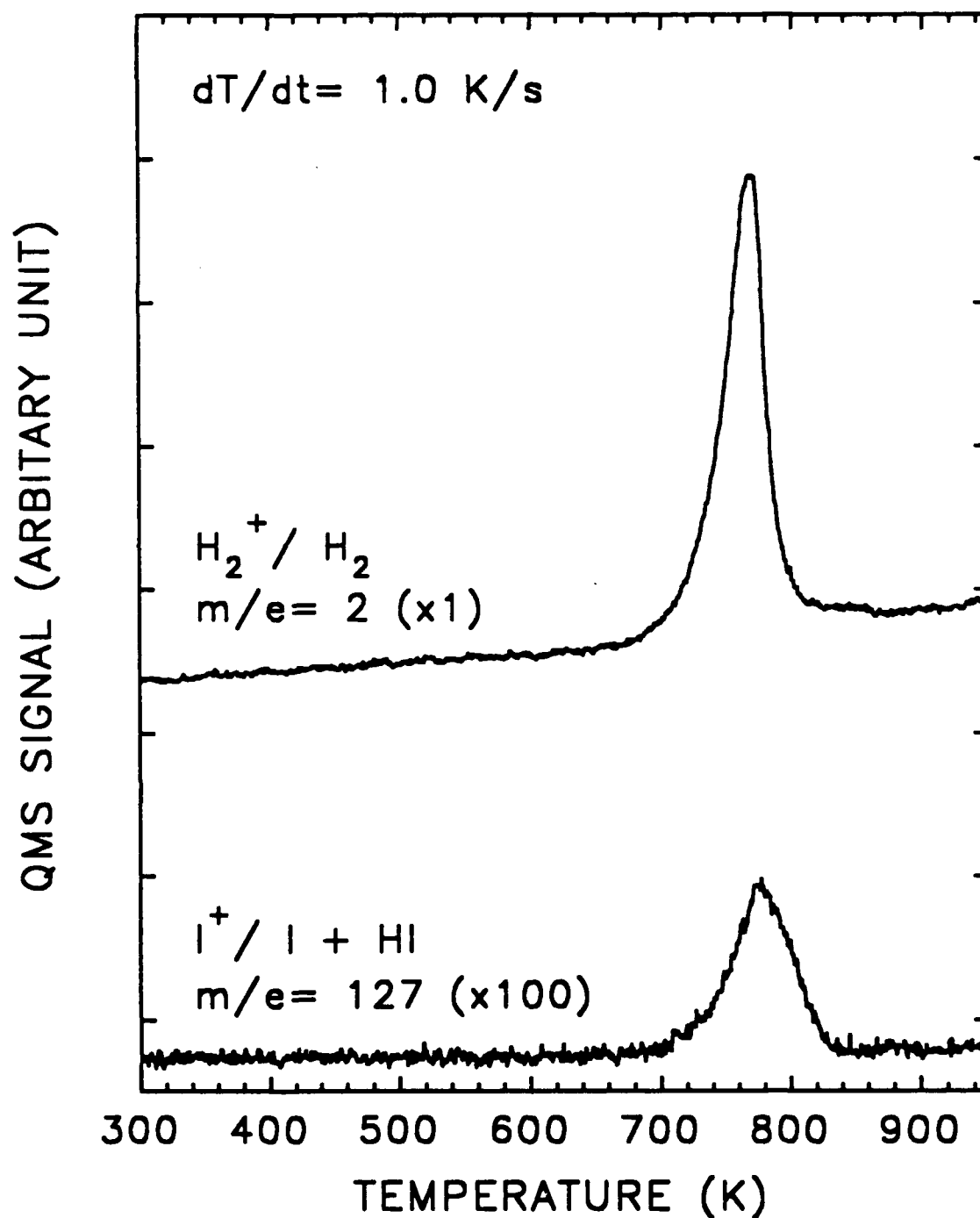
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Figure 2

Production of "Si-C" from Adsorbed $\text{HC} \equiv \text{CH}$



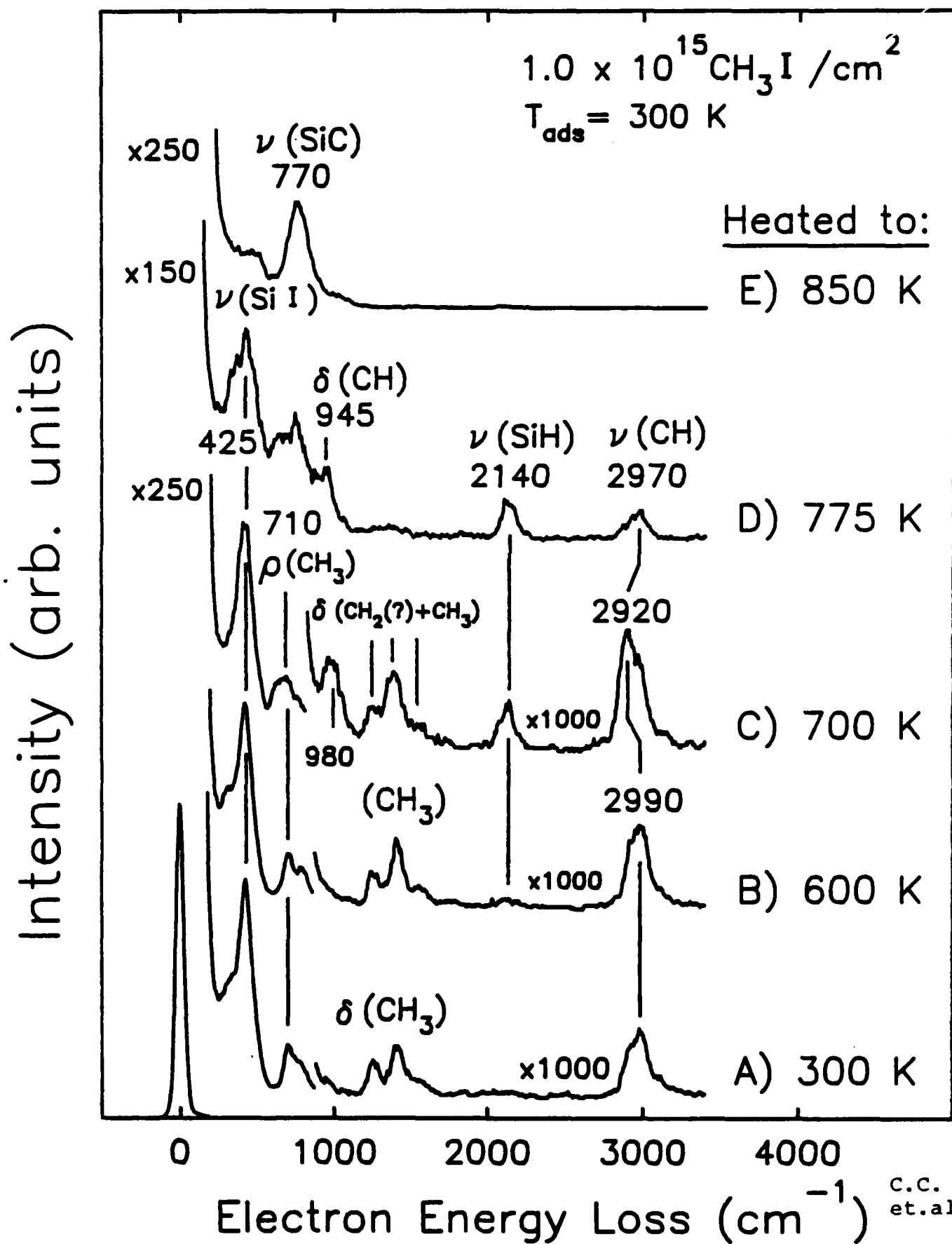
TYPICAL TPD SPECTRA FROM CH₃I ON Si(100)



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Figure 4

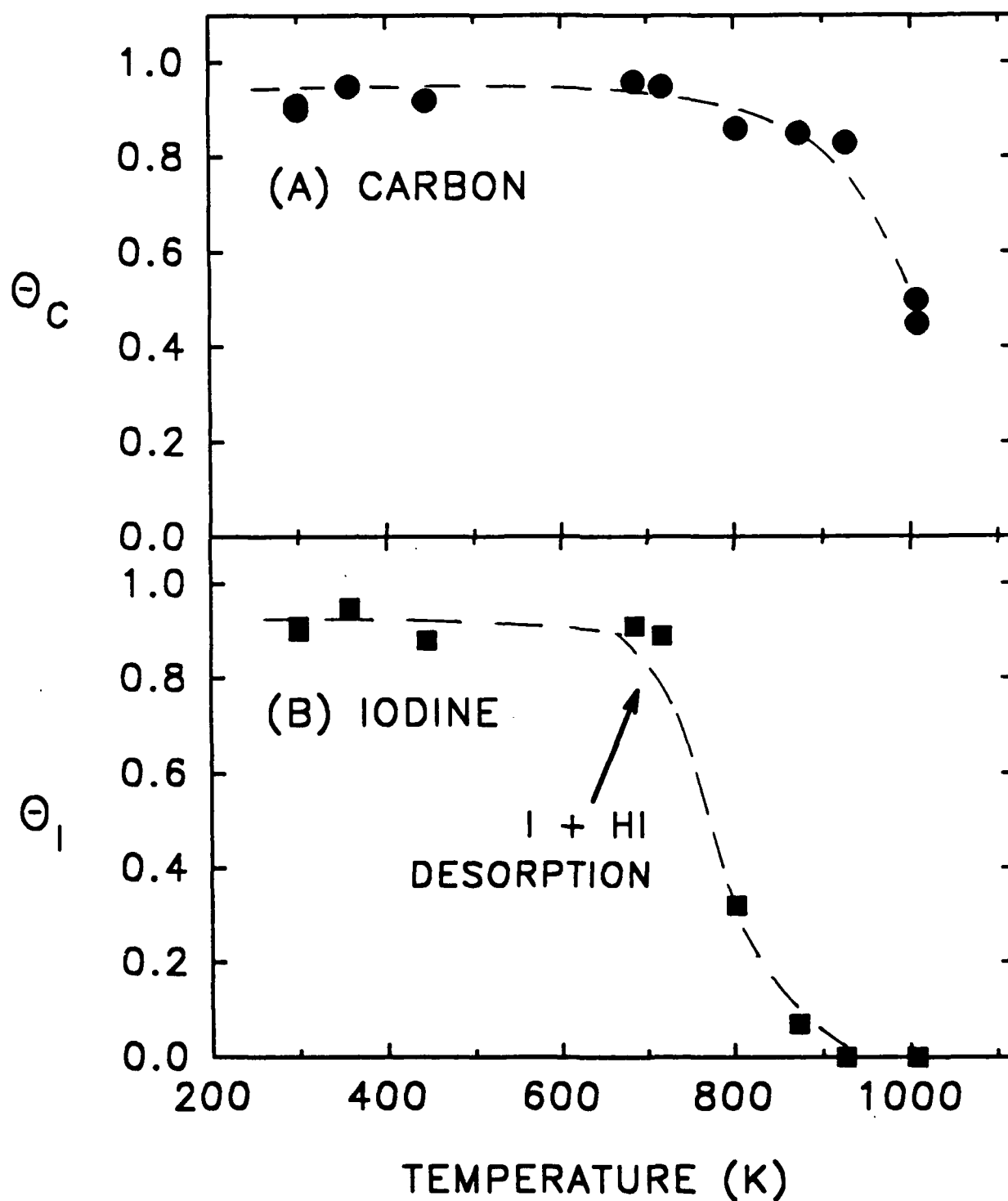
Thermal Decomposition of $\text{CH}_3(\text{a})$ on $\text{Si}(100)-(2\times 1)$



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Figure 5

THERMAL EFFECTS FOR CH_3I ON $\text{Si}(100)$ USING AUGER ELECTRON SPECTROSCOPY



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Figure 6

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